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QUANTITATIVE ANALYSIS OF AIRBORNE ASBESTOS BY X-RAY DIFFRACTION: FEASIBILITY STUDY

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Special x-ray diffraction geometry has been developed to distinguish chrysotile asbestos from serpentine and other clay minerals. The x-ray method requires alignment of the chrysotile fibers, and the technique for accomplishing this alignment has been developed and tested. A limit of detection of 0.2 μg asbestos has been achieved routinely for chyrsotile in the absence of extraneous material from real air samples.

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CONTENTS

INTRODUCTION 1

SPECIAL X-RAY DIFFRACTION GEOMETRY 2

SPECIMEN PREPARATION 5

RESULTS 8

DISCUSSION 9

REFERENCES 10

APPENDIX 11

FIGURES

1. (a) X-ray diffraction pattern from randomly oriented asbestos fibers 2

   (b) Diffraction pattern from a bundle with preferred orientation 2

2. Morphology of chrysotile asbestos 3

3. Standard diffractometer geometry 3

4. Special x-ray optics for quantitative measurement of aligned asbestos fibers 4

5. Backlighted macrograph of asbestos sample 5

6. Experimental arrangement of the ultrasonic "cell disrupter" 6

7. Special multielectrode grid used in the alignment of asbestos fibers 7

8. Photomicrograph of aligned asbestos sample 7

Quantit. tive Analysis of Airborne Asbestos

by X-Ray Diffraction.

Final Report on Feasibility Study

INTRODUCTION

The purpose of this report is to introduce a novel x-ray diffraction technique for the measurement of airborne asbestos. It has been recognized for some time that the determination of pollutant levels of asbestos by conventional x-ray diffraction is impractical for two primary reasons: 1.) The x-ray diffraction pattern of chrysotile (which comprises nearly 90% of all asbestos used worldwide) is almost identical to a number of clay minerals of similar chemical composition; 2.) at the concentration levels of interest the x-ray diffraction lines of asbestos are relatively weak and they occur in the presence of a very large background.

As is the case for all fibrous materials, the intensity of a specific diffraction peak of chrysotile or amphibole asbestos is enhanced if the fibers are aligned parallel to each other. Further, if the aligned fibers can be mounted on a suitably thin (low mass) substrate, the background (due to scattering of the incident x-ray beam) can be minimized. In order to investigate the applicability of the x-ray diffraction principle to the asbestos problem, a feasibility study was conducted which addressed the following questions:

1.) Can a scheme be devised for aligning small quantities of standard chrysotile fibers and mounting them on a low-mass substrate?

2.) Can a special x-ray diffraction geometry be developed which would be optimized for measuring these aligned fibers quantitatively?

Both parts of the task have been accomplished successfully for laboratory samples of chrysotile. The 3σ limit of detection for chrysotile standards is 0.2 μg for ten-minute measurements. Thus, the method appears feasible and ready for further development into a practical tool for quantitative analysis of source or ambient air samples.

SPECIAL X-RAY DIFFRACTION GEOMETRY

Chrysotile asbestos, like all crystals, has a characteristic x-ray diffraction pattern. However, platy serpentine has almost exactly the same x-ray pattern as chrysotile and many other clay minerals have very similar patterns. Therefore, preferred orientation of the chrysotile fibers offers the only hope of distinguishing chrysotile uniquely. Figures 1a and 1b show x-ray patterns from random orientation and preferred orientation, respectively. In a mixed sample of platy serpentine and chrysotile, the serpentine rings would be superposed on the chrysotile arcs. The net intensity due to chrysotile is obtained by measuring the intensity at the arc position (A in Figure 1), and subtracting the intensity of the ring at 90° to the arc, position B. This simple principle forms the basis for the method developed at the Naval Research Laboratory. But several factors make the problem difficult as will be described in the following paragraphs.

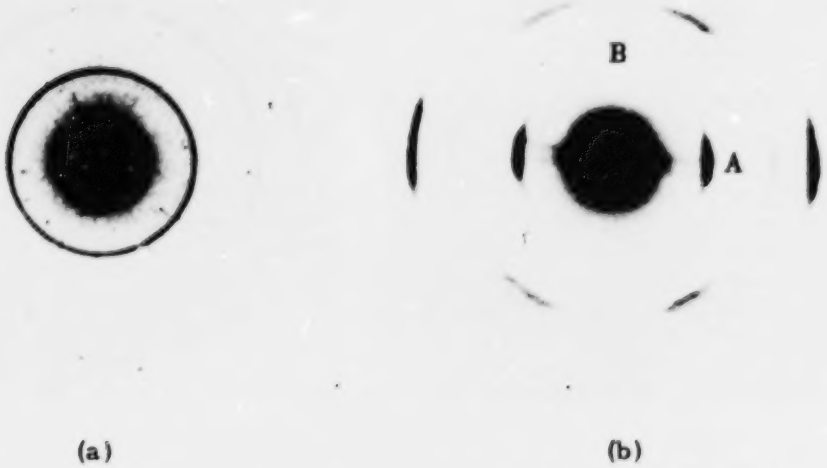

Figure 1. X-ray diffraction patterns (a) from randomly oriented asbestos fibers and (b) from a bundle with preferred orientation.

The first factor which makes measurement of asbestos difficult is that the quantity which can be collected from a reasonable amount of air is far too small to measure with x-ray film cameras. Therefore, diffractometers with electronic detectors are required, but this introduces a second difficulty because of the peculiar morphology of chrysotile. This morphology, which is that of a "rolled up" sheet of crystalline matter, is shown schematically in Figure 2. The a-axis of the monoclinic structure is parallel to the fiber axis; the c-axis is nearly perpendicular to the tube wall. Thus the axes b and c take

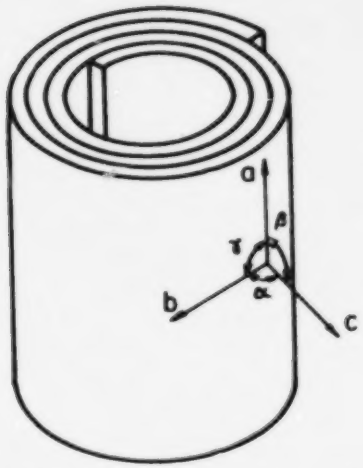

Figure 2. Morphology of chrysotile asbestos.
$\alpha = \gamma = 90^{o}$, $\beta = 93^{o}\ 16'$.

different orientations depending on where on the fiber they are set up. This means that standard diffractometer geometry cannot be used even with an oriented sample because the major crystal plane, (002), diffracts equally well for either orientation; see Figure 3. Therefore a special geometry was developed specifically for asbestos.

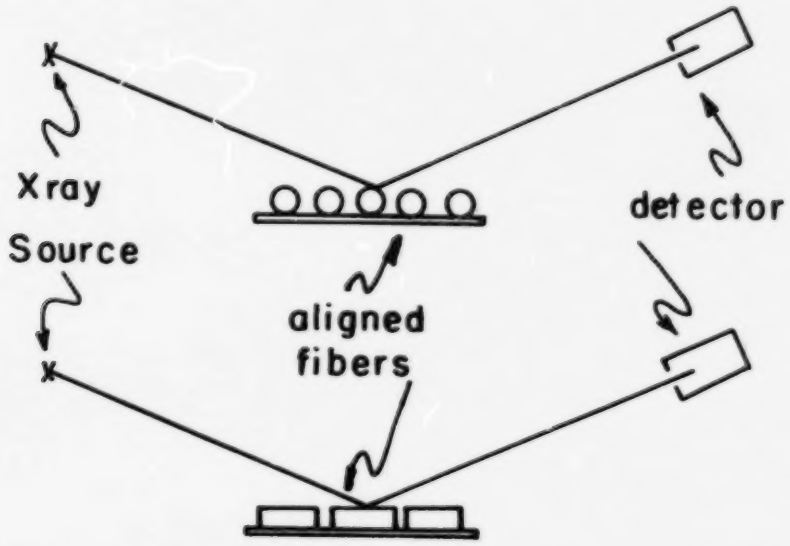

Figure 3. Standard diffractometer geometry. Diffraction from (002) planes is possible for all fiber rotations (where the axis of rotation is in the diffraction plane and perpendicular to fiber axis).

The geometry employed is shown schematically in Figure 4. Because of the manner in which the alignment is accomplished (described in the following section), the sample of asbestos is distributed over a circular area of about 1 cm diameter (as shown in Figure 5). In order to achieve diffraction from the entire sample, resulting in the highest signal, a large-cross-sectional-area x-ray beam is required;[1] in order to maintain good resolution, fine collimation is required. Figure 4 illustrates the use of a tubular-collimated broad x-ray beam from a spectrographic x-ray tube rather than a diffraction tube. The sample is mounted perpendicular to the x-ray beam to give an oriented pattern conceptually similar to Figure 1b. Using a chromium target x-ray tube the 2θ value for diffraction from (002) planes, $2d = 14.6$ Å, is 18°. By placing detectors at the two positions shown in Figure 4, the signal and background intensities are recorded simultaneously. During this feasibility study only one detector was available, so the signal and background were measured sequentially by rotating the sample 90° in its own plane between readings.

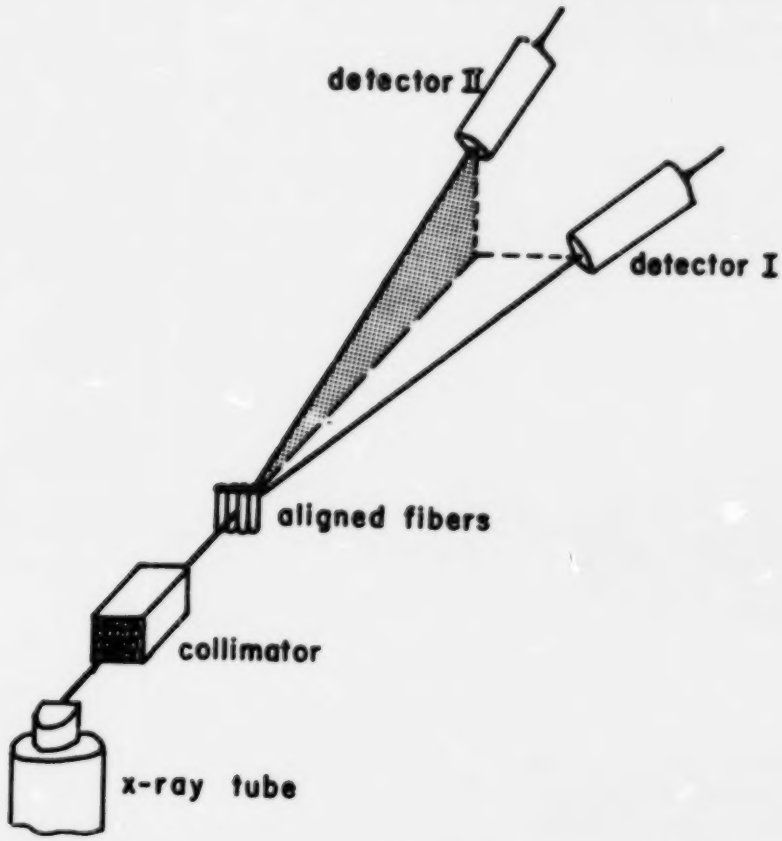

Figure 4. Special x-ray optics for quantitative measurement of aligned asbestos fibers.

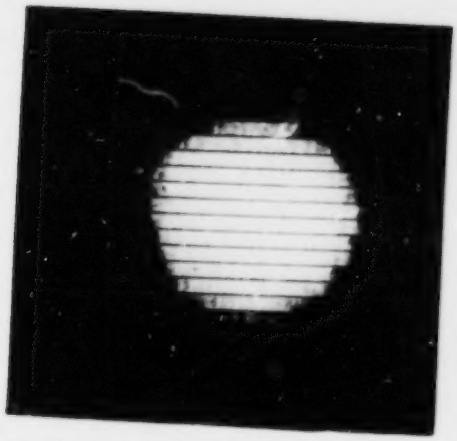

Figure 5. Backlighted macrograph of asbestos sample showing the distribution of aligned fibers on the multielectrode alignment grid; 3 x magnification.

SPECIMEN PREPARATION

Electrostatic alignment of asbestos fibers appeared to be the most obvious approach and had been suggested by an early patent. (2) This patent, however, concerned itself with bulk alignment of relatively large quantities of fibers in a liquid dielectric medium. For the small amounts of asbestos to be measured by the x-ray technique, the procedure described in reference 2 did not succeed in aligning the fibers completely enough to achieve optimum x-ray sensitivity nor was it possible to recover the specimen quantitatively from the alignment medium.

A significantly different alignment procedure (described below) was employed to produce a sample which was directly suitable for the x-ray measurements. Initial attempts did not accomplish adequate alignment, however, because of the "silky" nature of the chrysotile fibers. Breaking these "silky" fibers into straight fibrils was necessary if the full potential of the x-ray technique was to be realized. Ordinary ultrasonic cleaners were unsatisfactory, but the "cell disrupter" type, illustrated in Figure 6, succeeded in reducing the fiber size sufficiently.

Without going into detail on the numerous variations in sample preparation which were tried, the following procedure has been adopted and used successfully for orienting chrysotile standards:

Step 1. 3.0 mg of UICC standard Canadian chrysotile is placed in 1/2 ml of 1% aerosol OT solution in water. (The OT is necessary as a dispersing agent.) The suspension is sonicated for 45 minutes at 100 watts power using the cell disrupter as shown schematically in Figure 6.

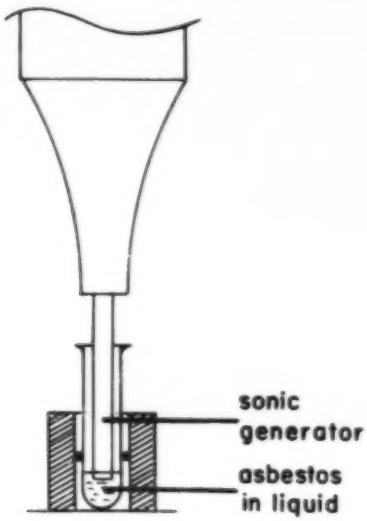

Figure 6. Experimental arrangement of the ultrasonic "cell disrupter" for reducing the size of the fibers.

Step 2. The sonicated suspension is diluted to 500 ml, making the asbestos concentration 6 μg/ml.

Step 3. A 25 ml aliquot of the diluted suspension (containing 150 μg of asbestos) is vacuum filtered onto a 25-mm disk of millipore.

Step 4. The millipore disk is folded and placed in a test tube and ashed for 2-1/2 hours in a low-temperature radio-frequency asher.

Step 5. 30 drops of a 0.001% solution of parlodion in distilled amyl acetate is added to the ashed residue, and the suspension is sonicated for 8 minutes to insure homogeneous distribution of asbestos.

Step 6. One drop of the suspension containing 5 μg asbestos is placed on a special grid, Figure 7, and 240 volts AC is applied to the electrodes (preparation of the grid is described in Appendix 1). It takes about 5 minutes for the amyl acetate to evaporate (the voltage is kept on the electrodes until evaporation is complete). Figure 5 shows the appearance of the dried sample, and Figure 8, at higher magnification, shows the alignment of the chrysotile fibers.

Step 7. A solution of 2.5% parlodion in amyl acetate is sprayed gently onto the dried sample to embed the fibers in a thin plastic film which can easily be removed by dipping the grid plate into water. This film has a mass density of about 60 $\mu g/cm^2$; the reason for wanting a thin film is to minimize the background intensity contributed by x-ray scattering from the film.

Figure 7. Special multielectrode grid used in the alignment of asbestos fibers. Interelectrode distance is approximately 0.8 mm.

Figure 8. Photomicrograph of aligned asbestos sample; 500 x magnification.

RESULTS

Seven inexperienced test subjects were selected to try out the alignment procedure as described above. Their results are shown in Table I.

TABLE I. MEASUREMENTS OF ASBESTOS STANDARDS

Analyst	Quantity of Asbestos per sample (μg)	Signal Above Background (c/s)	Background (c/s)	Sensitivity S (c/s/μg)	C_L^* (μg)
1	4.89	32.9	48.3	6.8	0.14
		27.9	63.0	5.7	0.18
		21.5	55.0	4.4	0.22
		30.3	55.5	6.2	0.16
2	4.38	23.3	44.5	5.3	0.17
		19.6	51.7	4.5	0.22
		30.7	36.9	7.0	0.12
3	4.75	32.9	54.5	6.9	0.14
		33.3	50.3	7.0	0.14
		21.4	39.5	4.5	0.19
		21.0	33.8	4.4	0.18
4	4.75	24.7	46.7	5.2	0.18
		25.9	54.4	5.4	0.18
		24.5	48.0	5.2	0.18
5	4.32	25.6	35.8	5.9	0.13
		28.4	33.4	6.6	0.12
		28.5	28.4	6.6	0.11
		27.9	35.2	6.5	0.12
6	4.75	32.9	35.4	6.9	0.11
		31.4	31.9	6.6	0.11
		31.2	36.4	6.6	0.12
7	4.75	23.1	45.0	7.0	0.13
		28.2	67.5	5.9	0.19
		24.4	59.1	5.1	0.20
	Average			5.9	0.16
	Relative Standard Deviation =			16%	

*Limit of Detection, C_L, from the Formula

$$C_L = 3\sqrt{N_B}/(S \times \text{Time}),$$

where N_B is the background over the counting interval, which conforms to the definition recommended by IUPAC. In this table, C_L is calculated for a 500-second counting interval.

DISCUSSION

The feasibility study has demonstrated that chrysotile asbestos can be aligned reproducibly and measured by x-ray diffraction. The sensitivity of the x-ray method is sufficient to give a limit of detection of 0.2 μg for 500 sec counting time; it is estimated that this figure may degrade to 0.4 or 0.5 μg for samples containing extraneous material.

The number of samples which can be analyzed in an eight-hour day using the special x-ray instrument depends primarily on the x-ray counting time. The total time per sample can be estimated by adding two minutes to the nine minutes counting time to record data and change the sample. This 11 minutes per sample would correspond to 44 samples in an eight-hour day.

It is germane, at this point, to estimate the costs and manpower necessary for a complete asbestos analysis laboratory. The prototype research instrument which is to be developed at NRL will be designed for the purpose of measuring individual asbestos samples and therefore will require the attention of the operating analyst; in a routine analytical laboratory, the procedure obviously should be automated. This would require modification of the prototype or perhaps fabrication of a second-generation instrument designed specifically for automatic operation. Assuming that forty samples per day is a reasonable work load for an automatic instrument, a two-person staff, both involved in all stages of sample preparation, should be adequate. At a labor and overhead cost of 200 dollars per day per staff member, the cost per sample would reduce to ten dollars. Sample preparation equipment (asher, filtration bands, sonicator, etc.) may have to be duplicated in order to avoid queuing delays.

The specific nature of the laboratory procedure will depend somewhat on the type of sample being measured (from an asbestos source or from ambient air). We assume at this time that all the critical questions regarding sample preparation have been resolved. "Source" samples will have a high ratio of asbestos to extraneous material (perhaps 1:1 to 1:10), while ambient air samples will have a smaller ratio (1:100 to 1:1000). In the former the removal of the extraneous material should not be as important as in the latter. On the other hand, "source" samples may contain a larger population of long, silky fibers which require longer sonication time before alignment; ambient air samples are less likely to contain these long fibers and long sonication can be avoided.

There are several uncertainties which must be investigated if the advantages of the x-ray method in speed and economy are to be exploited: First, the extraneous pollutant material which will be present in real air samples will affect the limit of detection because it will increase the scattered background signal. Second, the extraneous material may or may not affect the alignment of asbestos fibers or the

concentration of parlodion in the amyl acetate used as the alignment medium (preliminary tests indicate that alignment may be sensitive to parlodion concentration). Other effects, unknown at present, may have to be considered.

The next stage in the research program will be to collect particulate pollution from real air samples and spike it with known amounts of asbestos. These samples will be processed by the method developed in the feasibility study; variations in sample preparation may be required to achieve alignment of chrysotile in the presence of the extraneous material. Finally, unspiked air samples will be analyzed and the results compared with electron microscope measurements of the same samples.

It seems obvious that the x-ray method is applicable to asbestos in water as well as in air and to other forms of asbestos such as amphiboles; it should also be applicable to asbestos in food stuffs or other organic material which can be removed by ashing.

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(2) A. A. Winer and H. M. Woodrooffe, U. S. Patent No. 3,497,419, Feb. 1970.

(3) M. Fatemi and L. S. Birks, Multielectrode Apparatus and Technique to Prepare Aligned Asbestos Fibers on a Thin Substrate, NRL Patent-Disclosure Docket #8948, July 1974.

APPENDIX 1

Fiber alignment was accomplished by the use of a special multi-electrode grid.[3] Several considerations were important in the design of this device:

1.) The required electrostatic field for asbestos alignment in the medium ranges from 3000 to 5000 volts/cm.

2.) Because of the need to align the fibers in the plane of the substrate, it was necessary to incorporate thin (low profile) electrodes which would permit the liquid dielectric medium to spread freely over the surface. Initially a single pair of electrodes were used, about one centimeter apart. Such an arrangement causes a large population of fiber to align adjacent to the electrodes with virtually no asbestos in the center of the field. This observation led to the final configuration as shown in Figure 7. The relatively short distance between electrodes has the advantage of lower applied voltage, improving operational safety.

Fabrication procedure for these alignment grids is a standard technique used in microelectronics:

1.) A "master" is prepared ten times as large as the desired product and photoreduced on a quartz flat.

2.) Quartz discs with a 1200-Å layer of evaporated chromium are obtained either commercially or from a vacuum evaporation facility. Quartz is desirable because it cleans better than glass and vacuum deposition is more suitable than sputtering due to its more gentle treatment.

3.) The disks are sprayed with photoresist and baked.

4.) The original is placed in contact with the photoresist and exposed to ultraviolet light.

5.) The exposed disk is "developed" to remove the unexposed photoresist.

6.) The exposed chromium is etched away.

7.) The photoresist is dissolved and the grid is washed, dried, and inspected for continuity.